

JAPANESE

[JP,2000-191973,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS WRITTEN AMENDMENT

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the ink composition for aqueous ball pens. More particularly, it is related with a smooth feeling of a note, i.e., the ink composition for aqueous ball pens of shearing adhesiveness-reducing nature which are provided with the outstanding lubricity and fills cap-off nature, i.e., the drought resistance of a nib, writing performance, and preservation performance.

[0002]

[Description of the Prior Art]Conventionally, the oily ball-point ink which comprised an oily solvent system whose viscosity is about 10,000-20,000 cps as ball point ink, and the low viscosity aqueous-ball-pens ink which consists of an aqueous medium whose viscosity is about 10 cps are used widely. While said oily ball-point ink has an advantage which is a comparatively simple ball-point mechanism which is filled up with a direct liquid condition into a pipe shape ink seat part, and with which practical use is presented, without making an ink flow control member intervene, since a feeling of a note is heavy, it requires high writing pressure depending on the high viscosity of ink itself. Fault, like produce a skip phenomenon or a hand bleeds on the occasion of the note under what is called a BOTE phenomenon that ink accumulates in a writing tip part, and the environment where outside air

temperature is high tends to be produced for the mechanism which transfers the ink thin film in the high viscosity ink formed in balls faces to a writing surface. In said low viscosity aqueous ball pens on the other hand, While there was an advantage from which deep hand concentration is obtained by light writing pressure, the ink outflow control means for making low viscosity ink flow out properly, etc. needed to be arranged, it is obliged to a complicated structure which comprises many parts, and also the blot of a note and the Botha omission phenomenon tended to be produced depending on the low viscosity of ink.

[0003]Based on the above mentioned situation, the ink of the aquosity medium which gave thixotropy, i.e., the aqueous-ball-pens ink of shearing adhesiveness-reducing nature, is developed, and practical use came to be presented in recent years. At the time of the settlement to which shearing stress is not added, this kind of ink is hyperviscosity. By the high shearing by the ball which carries out a high velocity revolution if it is held stably and is in a ball-point mechanism at the time of a note. The ink to which only the ink near the ball hypoviscosity-ized, as a result ink passed through the gap of a ball and a ball seat part smoothly according to capillary force, ink transferred it to space, and said space transferred, Since it is released from shearing force, it will be in a hyperviscous state again and the blot phenomenon of the hand which was a fault of the conventional non-shearing adhesiveness-reducing nature aqueous ball pens will not be generated.

[0004]Some proposals about the above mentioned shearing adhesiveness-reducing nature aqueous-ball-pens ink are indicated. For example, the things (for example, a U.S. Pat. No. 4671691 gazette, JP,64-8673,B, etc.) using water-dispersion gum, resin, polysaccharide, etc. are mentioned. By the way, by the depolymerization operation by a microorganism, the disintegration by photochemical oxidation, and ***** operation of the chain by strong shearing force, the water-dispersion gum currently indicated by said gazette, resin, and polysaccharide thickener have the tendency to deteriorate or to be easy to deteriorate, and cannot say that the shearing adhesiveness-reducing nature effect is continuing stably. And said compound has the large viscosity change depending on temperature, and causes the Botha omission under the high situation of outside air temperature.

[0005]Although the things (JP,57-49678,A etc.) which used water-soluble synthetic high polymers, such as a constructed type acrylic resin of a bridge, as a shearing adhesiveness-reducing nature grant agent are indicated, Though a certain amount of shearing adhesiveness-reducing nature is presented as the characteristic of the constructed type acrylic resin of a bridge in the state of the hyperviscosity of thousands - about 10,000 cps of numbers, it is difficult to demonstrate the effect effectively on the occasion of application in the writing mechanism of aqueous ball pens. That is, a shearing adhesiveness-reducing effect is insufficient and viscosity change which does not not necessarily satisfy

balance with the increased viscosity required of the storage state at the time of hypoviscosity-ization produced according to the shearing force at the time of a note and un-writing down, and depends also for said compound on temperature is large.

[0006]Although the trials (JP,6-256699,A etc.) which use inorganic compounds, such as minerals particles, as a shearing adhesiveness-reducing nature grant agent are indicated, In particles like silicic anhydride particles, though it absorbs water and shearing adhesiveness-reducing nature is presented, it is dramatically difficult for the three-dimensional structure object of particles to pass through the narrow gap of a ball and a ball house stably in the homogeneous state, and it causes ink piece generating. Though the swelling clay like hydrophilic synthetic smectite is distributed to such detailed particles that it is substantially close to a solution state and shearing adhesiveness-reducing nature good in first stage is given, The phenomenon which separates and discharges water from a gel object temporally tends to happen, and there was a fault which produces separation of local ink and cutting of an ink pillar in a ball-point mechanism.

[0007]

[Problem(s) to be Solved by the Invention]This invention tends to cancel the fault of the above mentioned conventional ball point ink, tends to be provided with a smooth feeling of a note, and tends to provide the ink for shearing adhesiveness-reducing nature aqueous ball pens which fills cap-off nature, writing performance, and preservation performance.

[0008]

[Means for Solving the Problem]It is a general formula as a result of repeating examination wholeheartedly about ink for aqueous ball pens, in order that this invention persons may make the conventional fault solved. [Formula 1]Come out, chemical [as mechanical as the shown surface-active agent, and] and to a microorganism as the alkali swelling type acrylic emulsion which is a stable shearing adhesiveness-reducing nature grant agent, and a moisturizer Diethylene-glycol independence, Or by combining the mixture of ethylene glycol and a diethylene glycol, it finds out that aqueous-ball-pens ink excellent in writing performance and preservability is obtained, and came to complete this invention.

[Formula 1] $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_n\text{SO}_3\text{M}$ (as for R, the saturation of the carbon numbers 8-20 or unsaturated hydrocarbon, and n show an alkaline metal or ammonia, alkylamine, and alkanolamine among a formula, as for the integer of 3-30, and M.)

[0009]The ink composition for aqueous ball pens of this invention contains water, paints, a surface-active agent, a pH adjuster, a shearing adhesiveness-reducing nature grant agent, and a moisturizer as an essential ingredient, and said surface-active agent is a general formula.

[Formula 1]Come out, and are a compound expressed, and said shearing adhesiveness-reducing nature grant agent is a (**) alkali swelling type acrylic emulsion, and as said moisturizer with the mixture

of (**) diethylene-glycol independence or ethylene glycol, and a diethylene glycol. Three persons of these (b)s (**) (**) are contained. A pH adjuster is ammonia, amines, or an inorganic base, and pH is an ink composition for aqueous ball pens in which said moisturizer contains said shearing adhesiveness-reducing nature grant agent 20 to 50% of the weight 0.3 to 2.0% of the weight among all the constituents by solid conversion preferably in eight or more ink.

[Formula 1] $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_n\text{SO}_3\text{M}$ (as for R, the saturation of the carbon numbers 8-20 or unsaturated hydrocarbon, and n show an alkaline metal or ammonia, alkylamine, and alkanolamine among a formula, as for the integer of 3-30, and M.)

[0010]The surface-active agent used for the ink composition of this invention sticks to paints particles, since it has the lubricative improvement in a ball, i.e., the work which gives a smooth feeling of a note, at the same time it carries out the operation which distributes paints underwater, it does not need to add lubricant separately, and it is a general formula. [Formula 1]It comes out and pigment dispersibility and lubricity are excellent in the shown surface-active agent. Among a formula, when R exceeds less than 8 and 20, the purpose of this invention cannot be attained. as the example of said surface-active agent -- polyoxyethylene-lauryl-ether sodium sulfate (trade name: -- Aimard 20C.) E-27C, E-70C, and the above -- the Kao Corp. make and polyoxyethylene-alkyl-ether sodium sulfate (trade name: -- Aimard -- 20 CM) REBENORU WX, RATEMURU WX, and the above -- the Kao Corp. make and polyoxyethylene oleylethereal sulfate ester ammonium salt (trade name: -- the high tenor 08E.) 18E and the above -- polyoxyethylene-lauryl-ether sodium sulfate by Dai-Ichi Kogyo Seiyaku Co., Ltd. (trade name: -- NIKKOL SBL-2N-27, 3N-27, and 4N.) Made in Nikko Chemicals, Inc., polyoxyethylene-lauryl-ether sulfuric acid triethanolamine (trade name: SBL-2T-36, 4T, the above made in Nikko Chemicals, Inc.), etc. are mentioned above. If a cation form surface-active agent is used, the preservability of ink will be lost and lubricity or pigment dispersibility will lack in another polyoxyethylene-alkyl-ether phosphoric ester and anionic form surface-active agent and the Nonion type surface-active agent.

[0011]With an alkali swelling type acrylic emulsion used for an ink composition of this invention. An acid radical, for example, a carboxylic acid group, is contained in polymer by an acrylic unneutralized polymer emulsion, it swells by neutralizing with alkali, shearing adhesiveness-reducing nature is given, and a product made by primal ASE-60 loam and HASU and 28% of active principles are mentioned. . Swelling liquid of a salt produced by neutralizing said acrylic emulsion is the character of the water-soluble conventional acrylic mold thickener. Unlike effective shearing adhesiveness-reducing nature in thousands - a hyperviscous state of about 10,000 cps of numbers, demonstrate about 2000-cps shearing adhesiveness-reducing nature comparatively sufficient also by hypoviscosity, and have character similar to solution of gum which consists of a water-

soluble cellulose type derivative, and a natural resin like polysaccharide, but. It is dramatically stable to a depolymerization operation by a microorganism which are these faults, disintegration by photochemical oxidation, and a **** operation of a chain by strong shearing force. The aqueous-ball-pens ink using an emulsion of acrylic acid resin itself and viscosity change for which it already depends on temperature with water meltable types (JP,58-125770,A etc.) currently indicated in said gazette although it is publicly known are large, and cause the Botha omission of ink under a high situation of outside air temperature. A shearing adhesiveness-reducing nature grant agent used by this invention has a dramatically small viscosity change depending on temperature, and the Botha omission of ink does not happen easily under a high situation of outside air temperature. As the amount used, among an ink composition, it is 0.3 to 2.0% and is 0.6 to 1.5% more preferably in an active principle. In a smooth note being hard to be carried out to less than 0.3% of case and exceeding 2.0% on the other hand, it produces a tendency for viscosity of ink to rise and for an ink outflow from a nib to be checked.

[0012]Said acrylic emulsion is a fluid of hypoviscosity in acidic regions, by neutralizing this by ammonia, amines, or an inorganic base, an acrylic emulsion swells and thickening nature is given. However, if it returns to acidity again, since polymer will precipitate and ink will hypoviscosity-ize, in order to prevent this, it is necessary to use ammonia, amines, or an inorganic base as a pH adjuster, and to hold pH to or more 8 11 Suemitsu preferably eight or more. Although 11 or more may be sufficient as pH, character of polymer may change with warming.

[0013]A mixture of diethylene-glycol independence or ethylene glycol, and a diethylene glycol is preferably used 25 to 45% of the weight 20 to 50% of the weight to all the constituents as a moisturizer used for an ink composition of this invention. In less than 20% of the weight of a moisturizer or an ethylene glycol independent, there is a problem in cap-off nature. In addition, although glycerin, propylene glycol, etc. are known as a moisturizer which water color ink may be sufficient as and is used, If a mixture of these or these, and a moisturizer used by this invention is used, when it will become a cause of the Botha omission of ink in this invention and a moisturizer will exceed 50 % of the weight, there is a tendency for desiccation of a hand to become slow.

[0014]A kind in particular of paints used for an ink composition of this invention does not have restriction, and can use arbitrary things out of an inorganic system commonly used by water based ink composition conventionally and organic system paints. As inorganic system paints, titanium oxide, carbon black, and a metal powder are raised, for example. As an organic color, an azo rake, insoluble azo pigment, a chelate azo pigment, a phthalocyanine pigment, perylene and peri non paints, anthraquinone paints, a quinacridone pigment, a color rake, nitro paints, and nitroso paints are mentioned, for example. Specifically Copper phthalocyanine blue (C. I.74160), Phthalocyanine Green (C.

I.74260), Hansa Yellow 3G (C. I.11670), the dysazo yellow GR (C. I.21100), Paints usually used for various water color ink, such as the bar MANEN tread 4R (C. I.12335), brilliant carmine 6B (C. I.15850), and the Quinacridone red (C. I.46500), can be used.

[0015]A rust-proofer, an antiseptic, etc. which are used for usual by aqueous-ball-pens ink if needed can also be used for an ink composition of this invention, choosing them as it suitably.

[0016]Preparation of ink mixes the above-mentioned ingredient except an alkali swelling type acrylic emulsion and a pH adjuster, Usually, it can obtain easily by adding an acrylic emulsion, after distributing paints using dispersion machines known, such as a roll mill and a sand mill, adding a pH adjuster continuously, and swelling an acrylic emulsion.

[0017]While a water based ink composition of this invention has good ink appearance and there are no blur and line piece to space, it excels in cap-off nature, lubricity with the passage of time, and preservation performance. It is a general formula although Nonion or an anionic form surface-active agent is usually known by distribution of paints.

[Formula 1]It comes out and the shown surface-active agent has the stability of a system and two lubricative points. It has shearing adhesiveness-reducing nature equivalent to the gums which consist of a water-soluble cellulose type derivative, The preservation performance improves by leaps and bounds, leaving the advantage of gums by using alkali swelling type acrylic emulsion primal ASE-60 in which viscosity change for which it is stable and moreover depends on temperature to degradation and a microorganism is very small, and in the aforementioned system BOTA-proof omission, And the mixture of a point to a diethylene glycol or a diethylene glycol, and ethylene glycol of drought resistance is a uniquely effective moisturizer. Two persons of a surface-active agent and a shearing adhesiveness-reducing nature grant agent participate in stabilization of ink, and the shearing adhesiveness-reducing nature grant agent and the moisturizer are participating in the BOTA-proof omission nature from a pen body of aqueous-ball-pens ink. It is impossible to be able to obtain the water based ink composition which had the technical problem of this invention attained by the combination of the above-mentioned three-sort ingredient from the above thing, and to attain the technical problem in this invention by two person's combination or one person among these 3 persons.

[0018]Hereafter, although an example explains this invention still in detail, this invention is not limited at all by these examples. A translucent polypropylene tube 3 mm in inside diameter is filled up about ink obtained in the following examples, respectively, and it is a ballpoint pen tip made from stainless steel for commercial aqueous ball pens (a ball is the super-steel-alloys tungsten carbide, and). A **** ball-point was created for 0.5 mm in diameter, a written examination was done, and a storage stability examination of the Botha omission nature in the state where investigated a feeling of a brush and a skip state of a hand, and a nib was settled downward, and ink was also done. Although

the above result is shown in Table 1, it is as [evaluation / in front] follows.

1. Feeling of brush O : there is no feeling of jarring and it is smooth. a feeling of jarring was and x: was rough -- it feeling [of a brush] 2. becoming blurred, and by note of O:free hand. skip-less x: -- with [where a 3. Botha omission O:nib with a skip is settled downward by note of a free hand] no Botha omission -- the state where x:nib was settled downward -- 4with Botha omission. storage stability O: -- with a room temperature settlement article for one month. x without a viscosity difference with a 50 ** settlement article: The latter is hyperviscosity in a room temperature settlement article and a 50 ** settlement article for one month. [0019]Example 1 (black ink) paints: -- 7.0 % of the weight of carbon black (C. I.77265) dispersing agent, and lubricant: -- Aimard 20CM (polyoxyethylene-alkyl-ether sodium sulfate.) 1.5-% of the weight moisturizer by Kao Corp.: -- diethylene glycol . 15.0 % of the weight moisturizer: -- ethylene glycol . 18.0 % of the weight shearing adhesiveness-reducing nature grant agent: -- primal ASE-60 (alkali swelling type AKURIRUEMA RUJON and a product made by loam and HASU.) rust-proofer: -- benzotriazol 0.2 % of the weight antiseptic: -- pro cheating on the fare GXL (made by Zeneka Co.) 0.2 % of the weight Water 53.9 % of the weight 3.5 % of the weight of 28% active principles (active principle 1.0 % of the weight)

PH adjuster: Diethanolamine 1.2-% of the weight alkali swelling type acrylic emulsion, Target black ink was obtained by adding an acrylic emulsion, after distributing paints using a Sand grinder mill, mixing the above-mentioned ingredient except a pH adjuster, adding a pH adjuster continuously, and swelling an acrylic emulsion.

[0020]An ink composition was adjusted like Example 1 except having changed ethylene glycol in comparative example 1 Example 1 into glycerin.

[0021]An ink composition was adjusted like Example 1 except having changed a diethylene glycol in comparative example 2 Example 1 into ethylene glycol.

[0022]An ink composition was adjusted like Example 1 except having changed primal ASE-60 in comparative example 3 Example 1 into primal ASE-75 (alkali meltable type acrylic emulsion).

[0023]Example 2 (blue ink)

7.0 % of the weight of copper-phthalocyanine-blue (C. I.74160) NIKKOL SBL[]-4T (polyoxyethylene-lauryl-ether sulfuric acid TO RIETA Norian amine.) made in Nikko Chemicals, Inc. -- 4.0 % of the weight . Diethylene glycol 15.0 % of the weight Ethylene glycol 18.0 % of the weight Benzotriazol 0.2 % of the weight 0.2 % of the weight of pro cheating on the fare GXL Water 50.4 % of the weight Primal ASE-60 4.0 % of the weight (active principle 1.2 % of the weight)

Triethanolamine 1.2-% of the weight alkali swelling type acrylic emulsion, Target blue ink was obtained by adding an acrylic emulsion, after distributing paints using a Sand grinder mill, mixing the above-

mentioned ingredient except a pH adjuster, adding a pH adjuster continuously, and swelling an acrylic emulsion.

[0024]It is NIKKOL SBL-4T in comparative example 4 Example 2 Noy gene EA-170 (an ink composition was adjusted like Example 2 except having changed into the polyoxyethylene nonylphenyl ether and Dai-Ichi Kogyo Seiyaku Co., Ltd. make.)

[0025]An ink composition was adjusted like Example 3 except having changed primal ASE-60 in comparative example 5 Example 2 to high screw WAKO 104 (constructed type water solubility acrylic-acid-resin [of a bridge], Wako Pure Chem make) 0.3% of the weight.

[0026]Example 3 (red ink)

the Permanent Red 4R (C. I.12335) 7.0-% of the weight high tenor 08E (polyoxyethylene-lauryl-ether sulfate ester ammonium salt.) the Dai-Ichi Kogyo Seiyaku Co., Ltd. make -- 1.5 % of the weight Diethylene glycol 15.0 % of the weight Ethylene glycol 18.0 % of the weight Benzotriazol 0.2 % of the weight 0.2 % of the weight of pro cheating on the fare GXL Water 53.4 % of the weight Primal ASE-60. 3.5 % of the weight (active principle 1.0 % of the weight)

28% ammonia solution 1.2-% of the weight alkali swelling type acrylic emulsion, Target red ink was obtained by adding an acrylic emulsion, after distributing paints using a Sand grinder mill, mixing the above-mentioned ingredient except a pH adjuster, adding a pH adjuster continuously, and swelling an acrylic emulsion.

[0027]An ink composition was adjusted like Example 3 except having changed the 28% ammonia solution in comparative example 6 Example 3 into water.

[0028]An ink composition was adjusted like Example 3 except having changed the high tenor 08E in comparative example 7 Example 3 into sodium salt of a styrene acrylic copolymer.

[0029]

[Table 1]

例	筆感	カスレ	ボタ落ち	貯蔵安定性
実施例 1	○	○	○	○
実施例 2	○	○	○	○
実施例 3	○	○	○	○
比較例 1	○	○	×	○
比較例 2	○	○	×	○
比較例 3	○	○	○	×
比較例 4	×	×	○	○
比較例 5	×	×	○	○
比較例 6	○	○	×	×
比較例 7	×	×	○	×

[0030]

[Effect of the Invention]The result of Table 1 is excelled in cap-off nature, lubricity with the passage of time, and the preservation performance, while the water based ink composition of this invention has good ink appearance and there are no blur and line piece to space.

[Translation done.]